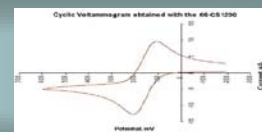


Analytical Electrochemistry: The Basic Concepts



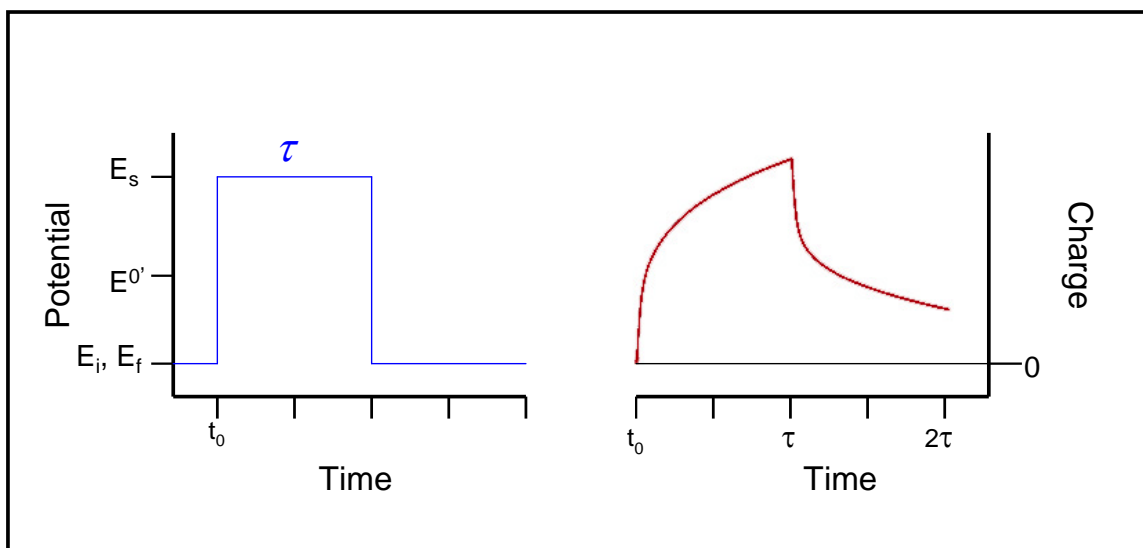
b) Chronocoulometry

In a chronocoulometry experiment, the total charge (Q) that passes during the time following a potential step is measured as a function of time. Q is obtained by integrating the current, i , during the potential step. For a well behaved system (diffusion only), the charge observed following a potential step to a point significantly more negative (for a reduction) of the E^0 , is described by the integrated Cottrell equation, known as the Anson equation

$$Q_d = \frac{2 n F A C_0 D_0^{1/2} t^{1/2}}{\pi^{1/2}}$$

The double potential step chronocoulometry experiment is illustrated in **Figure 12** for a diffusion-only redox system. Potential step programs in chronocoulometry are identical to those used in chronoamperometry. The most obvious advantage of recording charge rather than current is that Q increases with time following a potential step, reaching a maximum at the end of the step, where the most meaningful experimental data generally is observed.

Figure 12



Signal-to-noise improvements also result as the integration of the current signal tends to “smooth” the random noise contained in the signal. Hence, chronocoulometry is preferred over chronoamperometry for the measurement of electrode area (A) and diffusion coefficients (D).

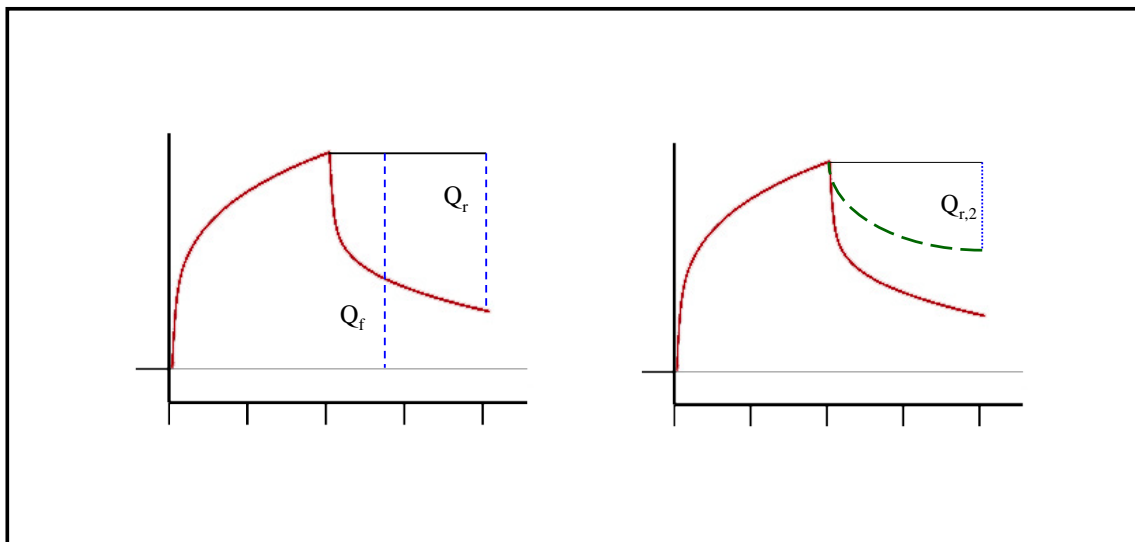
The enhanced signal observed in chronocoulometry also makes it the better technique for measurement of the kinetics of chemical reactions following electron transfer. In the double

potential step experiment illustrated in the previous figure, the reduced form of the redox couple still in the vicinity of the electrode following the forward step can be re-oxidized to the original material during the reverse potential step. As was the case in chronoamperometry, the signal observed in the reverse step is less than that seen in the forward step. The charge for a chemically and electrochemically reversible species on the reverse step is given by

$$Q_r = \frac{2 n F A C_0 D_0^{1/2}}{\pi^{1/2}} \left[\tau^{1/2} + (t - \tau)^{1/2} - t^{1/2} \right]$$

The values for charge measured at a time equal to $\tau/2$ after each step (designated Q_r and Q_f in the **Figure 13**) for such a system would yield a charge ratio $[Q_r(2\tau) / Q_f(\tau)]$ equal to 0.414. Chemical reactions coupled to the electron transfer will cause this ratio to deviate from the theoretical value. For example, if the reduced form of the species produced by the forward potential step decays to an electro-inactive species ($\text{Red} \xrightarrow{k} \text{P}$), the charge observed on the reverse potential step ($Q_{r,2}$, in **Figure 13**, at right) will be smaller than that for the uncomplicated case. Values for k , the homogeneous rate constant for the follow-up reaction, can be obtained using working curves derived for varying values of τ .

Figure 13



As was the case in chronoamperometry, a change in the applied potential of the working electrode will always be accompanied by a rearrangement of the ions in the double layer, leading to a contribution to the signal from capacitive current. Since the current is integrated over time in chronocoulometry, the charge due to the capacitive current will still be part of the total at the end of the step. The fact that it takes a very short amount of time after the potential step to charge the double layer does, however, allow the user to easily distinguish between the double layer charge, Q_c , and the charge due to diffusion, Q_d . If the total charge for the forward step, Q_f , equal to $(Q_d + Q_c)$, is plotted as a function of $t^{1/2}$, a straight line is obtained for a kinetically

uncomplicated system with an intercept equal to Q_c , and a slope of $(2 n F A C_0 D_0^{1/2} / \pi^{1/2})$. This is due to the double layer charging being essentially “instantaneous” following the potential step while the charge arising from diffusion requires time for the electroactive component to reach the electrode surface and react.

Perhaps the most important application of the chronocoulometric technique is the determination of surface concentrations of adsorbed electroactive species, designated Γ_0 . Following a forward potential step of sufficient magnitude, electroactive material that is adsorbed to the surface is instantaneously electrolyzed. The charge resulting from this reaction, Q_{ads} , being faradaic in nature is given by

$$Q_{ads} = n F A \Gamma_0$$

with Γ_0 having units of mol/cm^2 and other variables their usual meaning. The total charge observed (forward step) is now given by

$$Q_t = Q_d + Q_{ads} + Q_c = \frac{2 n F A C_0 D_0^{1/2} t^{1/2}}{\pi^{1/2}} + n F A \Gamma_0 + Q_c$$

When adsorbed materials are present, the intercept of the Anson plot becomes the sum of Q_{ads} and Q_c . While it is possible to ascertain a value for Q_c , and thus Q_{ads} , by running a “blank” electrolyte-only experiment, these measurements cannot accurately account for changes brought about by adsorption. A more suitable method for the determination of Q_{ads} involves double-potential step chronocoulometry.

Anson plots are prepared for both the forward and reverse potential steps, with Q_f vs. $t^{1/2}$ being plotted for the forward step and Q_r vs. $[\tau^{1/2} + (t - \tau)^{1/2} - t^{1/2}]$ for the reverse. For the case where the original material (Ox in this example) is adsorbed but the electrode product (Red) is not, the difference in the intercepts of the two plots directly yields Q_{ads} .

Figure 14 shows Anson plots for the forward potential step for a non-adsorbed analyte (left) and for a double-potential step experiment involving a pre-adsorbed material (right).

Figure 14

